10/500305

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 25 MAR 2004
WIPO PCT

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
9461		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB 02/05455	04.12.2002	02.01.2002
International Patent Classification (IPC) or both national classification and IPC		
C07C67/05		
Applicant		
BP CHEMICALS LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11.07.2003	24.03.2004
Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Lorenzo Varela, M.J. Telephone No. +49 89 2399-8239

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB 02/05455

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-6, 8-10, 12-17	as originally filed
7, 11	received on 18.12.2003 with letter of 17.12.2003

Claims, Numbers

1-18	as originally filed

Drawings, Sheets

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	3-7
	No:	Claims	1,2,8-18
Inventive step (IS)	Yes:	Claims	
	No:	Claims	3-7
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item I

Basis of the report

The present report is established on the application as originally filed with the amendments on pages 7 and 11 provided with letter dated 17.12.03. The applicant argues that the subject-matter of the claims is novel and inventive because in step d) of claim 1, the product stream from the vinyl acetate is separated by distillation **together with** at least some of the acetic acid/water stream produced from the oxidation reactor and he draws the attention of the Examining Division to tables 2 and 3 to show that feeding a combined stream of vinyl acetate, acetic acid and water (stream i) and a stream of acetic acid and water (stream ii) to the distillation column, the concentration of ethyl acetate by-product in the vinyl acetate product stream is reduced.

However, the applicant's attention is drawn to the fact that the technical feature that in step d) of claim 1, the product stream from the vinyl acetate is separated by distillation **together with** at least some of the acetic acid/water stream produced from the oxidation reactor is not drafted in the present claim 1; claim 1 reads: "... d)separating at least a portion of the product stream from step c) and at least a portion of the carboxylic acid and water fraction produced in step b) by azeotropic distillation into an overhead fraction comprising alkenyl carboxylate and a base fraction comprising carboxylic acid". The separation as disclosed in present claim can be carried out separately for both product streams from steps b) and c). Hence, the objections raised in the written opinion are maintained as shown below.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

D1: US-A-6143921
D2: US-A-6040474
D3: EP-A-0985656

1. The present application relates to an integrated process for the production of an alkenyl carboxylate like vinyl acetate which comprises: a)contacting in an oxidation zone a C2-C4 alkane, like ethane, a molecular oxygen containing gas and optionally

the corresponding alkene and water in the presence of a catalyst; b)separating the product stream into a fraction comprising the alkene and a fraction comprising a carboxylic acid and water, c)contacting the alkene fraction, a carboxylic acid and oxygen with a catalyst in a second reaction zone to produce a product stream comprising alkenyl carboxylate, water and carboxylic acid; d)submitting the product streams from steps c) and the carboxylic acid and water fraction from step b) to azeotropic distillation and e)recovering the alkenyl carboxylate from step d).

Novelty

2. The subject-matter of claims 1, 2 and 8-18 is not novel in the sense of Art. 33(2) PCT. Document D1 discloses an integrated process for the production of vinyl acetate, comprising: a)contacting ethane, oxygen, ethene and water in the presence of a catalyst; b)separating the product stream into a fraction comprising ethylene and a fraction comprising acetic acid and water, c) contacting the ethylene fraction, acetic acid and water in the presence of a catalyst for the production of vinyl acetate, d)submitting the streams from c) and b) to azeotropic distillation and e) recovering vinyl acetate (see the passages mentioned in the search report). This disclosure is novelty destroying for the subject-matter of the above-mentioned claims.

3. The subject-matter of claims 3-7 is novel in the sense of Art. 33(2) PCT. The specific operation conditions disclosed in the claims (the facts of mixing the product streams from steps a) and c) and submitting them to distillation) are not disclosed in the available prior art.

Inventive step

4. The subject-matter of claims 3-7 cannot be considered as involving an inventive step in the sense of Art. 33(3) PCT.

4.1. Processes for the production of vinyl acetate differing from the presently claimed process in the fact of mixing the product streams from steps a) and c) and submitting them to distillation are known in the state of the art (documents D1-D3; see the passages mentioned in the search report).

4.2. The fact of combining both streams before subjecting them to distillation is merely

one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed. An inventive step can only be acknowledged if examples are provided showing that unexpected effects are obtained when carrying out this step. However, an evidence of such unexpected effects is not available at the moment taking into account that according to page 3, lines 12-20 and example I-model B, a reduction in one of the by-products is obtained if the stream obtained in step b) containing acetic acid and water is combined with the stream from step c) before submitting them to distillation but there is no evidence of a reduction of by-products if a part of the stream from step a) is used instead of the stream obtained in step b) and containing acetic acid and water. Therefore, an inventive step cannot be acknowledged.

Further comments

5. The terms "the contents of which are hereby incorporated by reference" used on pages 4 and 9 render unclear the scope of the protection sought, contrary to Art. 6 PCT. These terms should not have been used.

6. The use of the word "about", especially in connection with numerical ranges, is generally regarded as rendering the determination of the exact scope of the range difficult. When used in a claim as well as in the description, this results in lack of clarity, contrary to Art. 6 PCT. Therefore, this word should not have been used in the description even if it was used to refer to the prior art.

7. The vague and relative terms "substantially", "essentially" and "approximately" used in the description have no generally accepted meaning in the art and are regarded as unclear, contrary to Art. 6 PCT.

8. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D1 is not mentioned in the description, nor is this documents identified therein.

or more of nitrogen, argon, methane, carbon dioxide, carbon monoxide, hydrogen, and low levels of other C_2-C_4 alkenes/alkanes.

Suitably, the concentration of alkene (as fresh feed and/or recycle component) is from 0 and up to and including 50 mol % of the total feed, including recycles, to the oxidation reaction zone, preferably from 1 to 20 mol %, more preferably from 1 to 15 mol %.

Suitably, the concentration of water (as fresh feed and/or recycle component) is from 0 to 50 mol % inclusive of the total feed, including recycles, to the oxidation reaction zone, preferably from 0 to 25 mol %.

In a preferred embodiment of the present invention, an alkene, such as ethylene, and water are co-fed into the oxidation reaction zone.

Suitably, the alkene, for example, ethylene, and water may be used in a ratio of 1 : 0.1-250 by weight, such as 1 : 0.1-100 or 1 : 0.1-50 but preferably in a ratio 1 : 0.1-10 by weight.

When solid catalysts are used in the oxidation reaction zone, the alkane, the optional corresponding alkene, molecular-oxygen containing gas, optional water and any recycle gases are preferably passed through the oxidation reaction zone with a residence time corresponding to a combined gas hourly space velocity (GHSV) of 500-10,000hr^{-1}; the GHSV being defined as volume (calculated at STP) of gas passing through the reactor divided by the bulk volume of settled catalyst.

The oxidation reaction of the present invention may suitably be carried out at a temperature in the range from 100 to 400°C, typically in the range 140 to 350°C.

The oxidation reaction of the present invention may suitably be carried out at atmospheric or superatmospheric pressure, for example, in the range from 80 to 400 psig. / (0.65 to 2.86 MPa).

Typically, alkane conversions in the range 1 to 99% may be achieved in the oxidation reaction of the present invention.

Typically, oxygen conversions in the range 30 to 100% may be achieved in the oxidation reaction of the present invention.

In the oxidation reaction of the present invention, the catalyst suitably has a productivity in the range 10 to 10000 grams of carboxylic acid, such as acetic acid, per hour per kilogram of catalyst.

fresh and recycle acid.

The carboxylic acid fed to the second reaction zone for the production of alkenyl carboxylate may comprise at least a portion of the acid obtained from downstream processes such as from the separation of the acid from a mixture of the acid/alkenyl carboxylate/water.

The carboxylic acid fed to the second reaction zone, such as acetic acid, has a water content, such that the amount of water entering the second reaction zone preferably comprises less than 6 wt%, more preferably less than 4 wt%, especially less than 3 wt% of the total carboxylic acid and water entering the second reaction zone.

At least part of the carboxylic acid fed to the second reaction zone may be liquid.

When solid catalysts are used in the second reaction zone for the production of alkenyl carboxylate, the product from the oxidation reaction zone, any additional alkene or carboxylic acid reactants, any recycle streams and molecular oxygen-containing gas are preferably passed through the second reaction zone at a combined gas hourly space velocity (GHSV) of 500 to 10,000hr^{-1}.

The second reaction zone for the production of alkenyl carboxylate may suitably be operated at a temperature in the range from 140 to 200°C.

The second reaction zone for the production of alkenyl carboxylate may suitably be operated at a pressure in the range 50 to 300 psig (0.44 to 2.17 MPa).

The second reaction zone for the production of alkenyl carboxylate may suitably be operated as either a fixed or a fluidised bed process.

Carboxylic acid conversions in the range 5 to 80% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

Oxygen conversions in the range 20 to 100% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

Alkene conversions in the range 3 to 100% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

In the second reaction zone for the production of alkenyl carboxylate, the catalyst suitably has a productivity in the range 10 to 10000 grams of alkenyl carboxylate per hour per kg of catalyst.

The product stream from the second reaction zone comprises alkenyl

10/520305

Box No. VIII (iv) DECLARATION: INVENTORSHIP (only for the purposes of the designation of the United States of America)

The declaration must conform to the following standardized wording provided for in Section 214; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iv). If this Box is not used, this sheet should not be included in the request.

Declaration of inventorship (Rules 4.17(iv) and 51*bis*.1(a)(iv)) for the purposes of the designation of the United States of America:

I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.

This declaration is directed to the international application of which it forms a part (if filing declaration with application).

This declaration is directed to international application No. PCT/..... (if furnishing declaration pursuant to Rule 26*ter*).

I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.

I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications," by application number, country or Member of the World Trade Organization, day, month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.

Prior Applications: GB Application No. 0200021.4 dated 2nd January 2002

I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name: CLARKE, Robert William

Residence: Driffield, United Kingdom
(city and either US state, if applicable, or country)

Mailing Address: 28 Hymers Close, Brandesburton, Driffield, East Riding of Yorkshire, YO25 8SQ, United Kingc

Citizenship: English

Inventor's Signature: ..... Date: .....
(if not contained in the request, or if declaration is corrected or added under Rule 26*ter* after the filing of the international application. The signature must be that of the inventor, not that of the agent)

(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26*ter* after the filing of the international application)

Name: ROBERTS, Mark Stephen

Residence: Beverley, United Kingdom
(city and either US state, if applicable, or country)

Mailing Address: 23 Danesway, Beverley, East Yorkshire, HU17 7JQ, United Kingdom

Citizenship: British

Inventor's Signature: ..... Date: .....
(if not contained in the request, or if declaration is corrected or added under Rule 26*ter* after the filing of the international application. The signature must be that of the inventor, not that of the agent)

(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26*ter* after the filing of the international application)

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iv)".